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Products of Thermal Degradation of Dielectric Fluids

Midwest Research Inst., Kansas City, MO

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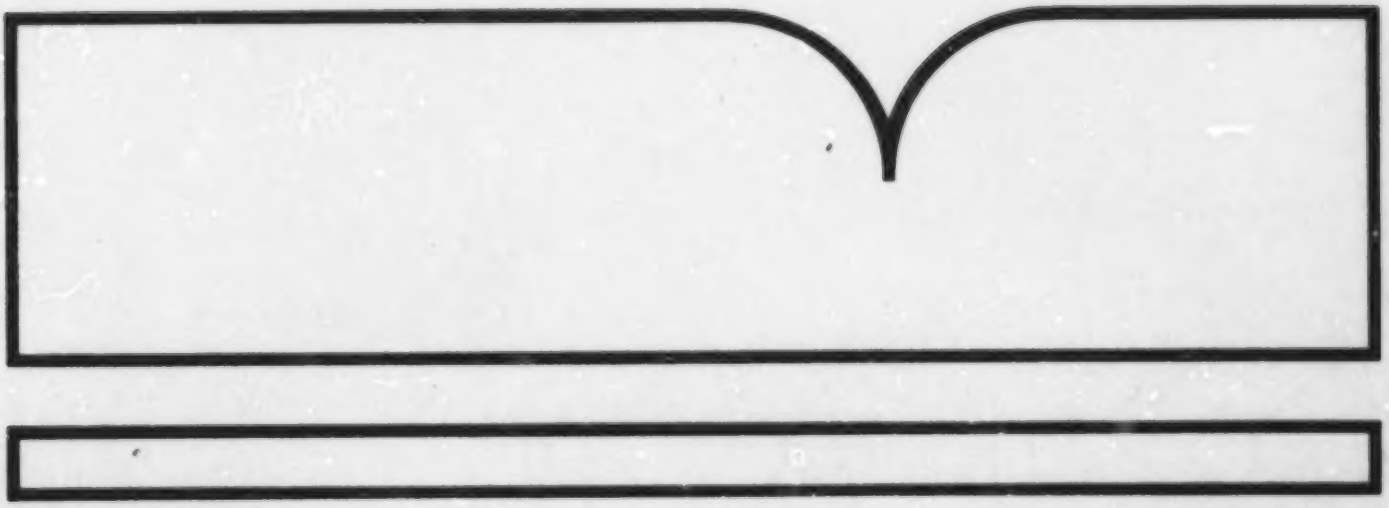

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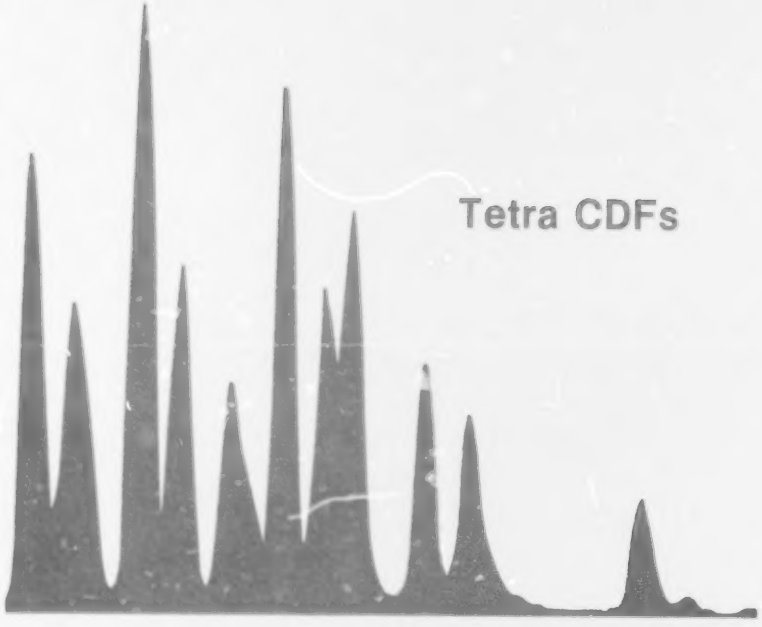

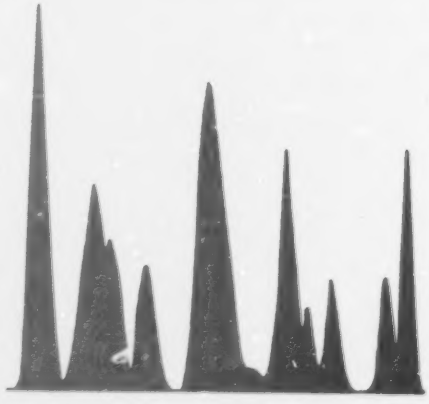

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16. ABSTRACT This report describes the results of a series of experiments which were conducted to augment the data presented in a previous report (EPA 560-5-84-009). The work presented here includes both repeat runs of those previously reported and also investigations of materials not previously tested. The results of the repeat runs correlate well with the previously reported results. The formation of PCDFs and PCDDs from the PCB-spiked mineral oil, as well as the calculated destruction efficiencies for PCBs, closely match the previously reported results. The repeat chlorobenzene runs show higher levels of PCDF and PCDD formation than previously. However, several concentrations in the previous report are "greater than" values; hence, comparison is difficult. Significant amounts of PCDFs and PCDDs were formed from the tetrachloroethylene fluid. The two high temperature hydrocarbon fluids did not produce PCDFs or PCDDs. It appears that, under these thermal destruction conditions, the extent of PCDF formation varies among dielectric fluids by several orders of magnitude. The highest PCDF formation was noted for PCB-containing dielectric fluids (about 0.01% of the amount fed), trichlorobenzene had about 5×10^{-4} conversion efficiency, and the least formation was observed in tetrachloroethylene (about 4×10^{-6}). It should be noted that the thermal combustion system was optimized for PCDF formation from PCBs and the optimal conversion conditions for the other fluids may produce higher PCDF yields. The results for the OCDF-spiked feed oil runs showed formation of a number of lower chlorinated PCDF homologs with a variety of isomers within each homolog.

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PRODUCTS OF THERMAL DEGRADATION OF DIELECTRIC FLUIDS

By

Stephen E. Swanson
Mitchell D. Erickson
Leslie Moody

WORK ASSIGNMENT NO. 23

INTERIM REPORT NO. 2

EPA Contract No. 68-02-3938
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May 23, 1985

For

U.S. Environmental Protection Agency
Office of Toxic Substances
Field Studies Branch, TS 798
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PREFACE

This report presents the results of a portion of Work Assignment No. 23 on U.S. Environmental Protection Agency Contract No. 68-02-3938, "Incineration Testing of PCBs." The work was done at Midwest Research Institute (MRI) during the period September 28, 1984, to January 28, 1985. This work was performed as a follow-up to work presented previously in "Thermal Degradation Products From Dielectric Fluids," by Mitchell D. Erickson, Christopher J. Cole, Jairus D. Flora, Jr., Paul G. Gorman, Clarence L. Haile, Gary D. Hinshaw, Fred C. Hopkins, and Stephen E. Swanson, Interim Report No. 1 on this work assignment, November 19, 1984 (Report No. EPA-560/5-84-009). Mitchell D. Erickson was the MRI Work Assignment Leader. This report was prepared by Dr. Erickson, Stephen E. Swanson and Leslie Moody. The thermal combustion system was operated by Gary D. Hinshaw, Christopher J. Cole, Paul G. Gorman, and Fred C. Hopkins. Laboratory work was done by Mr. Swanson and Ms. Moody. The GC/MS data were acquired by John Gamble, Jon Onstot, Gil Radolovich, and Margaret Wickham. Mass spectral data were interpreted by Dr. Erickson, Mr. Swanson and Ms. Moody.

The EPA Work Assignment Manager, Daniel T. Heggem of Field Studies Branch, provided helpful guidance and advice.

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I. INTRODUCTION

The Environmental Protection Agency (EPA) has issued an Advance Notice of Proposed Rulemaking (ANPR) (USEPA 1984a) and proposed rule (USEPA 1984b) to gather data on the specific risks posed by fires involving electrical transformers that contain polychlorinated biphenyls (PCBs) and also on mechanisms for mitigating or eliminating these risks. A work assignment was issued to Midwest Research Institute (MRI) to support EPA's data-gathering activities under the ANPR. Specifically, MRI was asked to study the combustion of transformer dielectric fluids to investigate the potential for formation of toxic products such as polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs). A report (Erickson et al. 1984) presents the results of previous work completed on this work assignment.

This report describes the results of a series of experiments which were conducted to augment the data presented in the previous report (Erickson et al. 1984). The work presented here includes both repeat runs of those previously reported and also investigations of materials not previously tested. The next section presents a summary of the results. Section III presents the experimental methods. Section IV presents the results of the tests performed with the dielectric fluids.

II. SUMMARY

Two types of experiments were performed during Phase IV of this project. First, a series of repeat runs were made under identical conditions to those previously reported (Erickson et al. 1984). In these runs, the feed oil was mineral oil spiked with individual PCB congeners as in Phase II, and mineral oil spiked with Aroclor 1254 as in Phase III. Also during Phase IV, repeat runs were made using a trichlorobenzene dielectric fluid. The second group of Phase IV runs were performed to investigate PCDF and PCDD formation from the combustion of other non-PCB containing dielectric fluids which had not previously been tested. The three dielectric fluids which were tested were tetrachloroethylene (Wecosol®), a paraffinic high temperature hydrocarbon (RTEmp®), and an esterified high temperature hydrocarbon (Dielectric fluid HT-310-S). Finally two runs were made in which the feed oil consisted of mineral oil spiked with octachlorodibenzofuran (OCDF). These runs were made to better characterize the chemistry of PCDF formation.

The results of the repeat runs correlate well with the previously reported results. The formation of PCDFs and PCDDs from the PCB-spiked mineral oil, as well as the calculated destruction efficiencies for PCBs, closely match the previously reported results. The repeat chlorobenzene runs show higher levels of PCDF formation than in Phase III. However, several concentrations in the previous report are "greater than" values; hence, comparison is difficult.

Significant amounts of PCDFs and PCDDs were formed from the tetrachloroethylene fluid. The two high temperature hydrocarbon fluids did not produce PCDFs or PCDDs. Figure 1 summarizes the conversion efficiency of dielectric fluid to PCDF for the different dielectric fluid types tested in Phases III and IV. It appears that, under these thermal destruction conditions, the extent of PCDF formation varies among dielectric fluids by several orders of magnitude. The highest PCDF formation was noted for PCB-containing dielectric fluids, and the least formation was observed in tetrachloroethylene. It should be noted that during Phase II the thermal combustion system was optimized for PCDF formation from PCBs. The results for the OCDF-spiked feed oil runs showed formation of a number of lower chlorinated PCDF homologs with a variety of isomers within each homolog.

III. EXPERIMENTAL METHODS

A. Thermal Combustion System

1. Description

MRI has developed a bench-scale thermal combustion test system which can be used to examine various combustion processes. It has also been used to provide data on the incinerability (i.e., destruction efficiency) of hazardous compounds in solid or liquid waste material, and to provide data on products of incomplete combustion that may be formed. This system can provide combustion data on gram-quantity samples of materials in either solid or liquid form or even semisolid materials, such as tars. In contrast, other related systems often can handle only very small quantities of pure compounds.

The system is described in detail in a previous report which presents the results of previous work on this work assignment (Erickson et al. 1984). Briefly, the system consists of a volatilizing/pyrolysis heater for the sample, an air preheater furnace, and the main combustion furnace (all electrically heated). Separate volatilization/pyrolysis furnaces are used for solid/semisolid feed and for liquid feed. Gas flow through the combustion furnace is laminar and can be varied to provide different gaseous residence times. The combustion temperature can also be varied, up to a maximum of 1200°C (2200°F). The liquid feed rate, which is controlled by a syringe pump, can be varied over a nominal range of 1 µL/min to 1 mL/min.

Primary operating conditions that can be varied and controlled in this system are temperature, oxygen concentration, and residence time. For this program, the system has been operated using continuous injection of liquid feeds.

The O_2, CO_2, and CO concentrations in the effluent gases were continuously monitored during each run. Semivolatile organic compounds were also collected in the effluent stream by adsorption and concentration in an XAD-2 sampling trap.

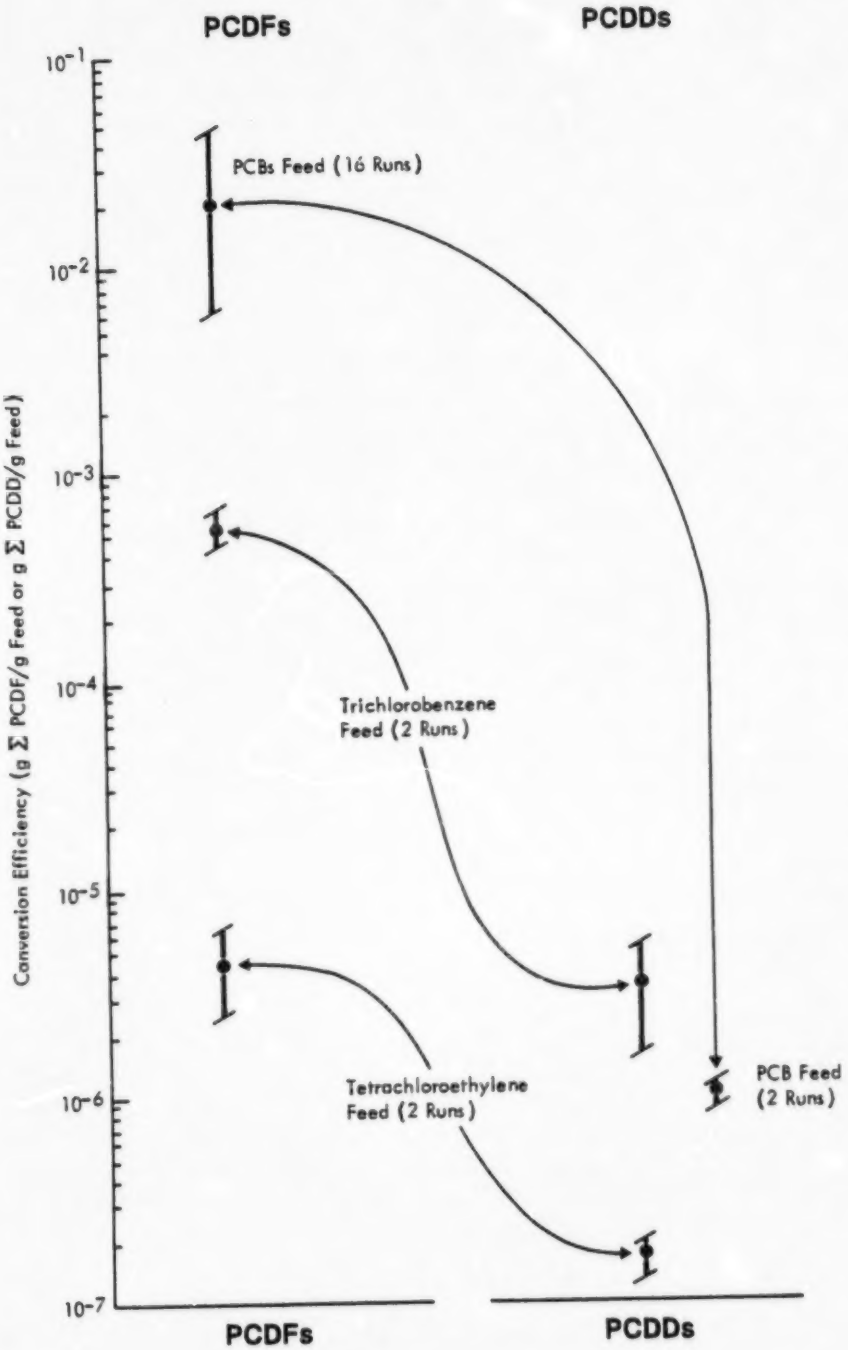

Figure 1. Summary of conversion efficiencies for total PCDFs from Phase III and Phase IV runs.

2. Operating Conditions

The pertinent operating conditions are listed in Table 1. The thermal combustion system was operated under the conditions optimized for PCDF formation from PCBs and used in all of the Phase III experiments described previously (Erickson et al. 1984). However, it is recognized that the optimal conditions for PCDF formation from other compounds are probably different. The key operational parameters were a combustion temperature of 675°C, with a residence time of 0.8 s, with 8% excess oxygen. All samples were fed at a rate of 14 µL/min.

B. Chemical Analysis

Samples were analyzed as described in the previous report (Erickson et al. 1984). Each effluent sample consisted of two parts, the XAD-2 resin cartridge and a solvent rinse of the sample collection apparatus. The XAD-2 samples were spiked with ^{13}C-surrogates and Soxhlet-extracted. This extract was combined with the associated solvent rinse to make a combined effluent extract. The combined extract was evaporatively concentrated to 2 mL. One-half of each extract was cleaned by chromatography on acidified silica and acidified alumina. The cleaned extracts were analyzed for PCDFs and PCDDs. The remaining extract aliquot was analyzed for PCBs. Some of these extracts were also screened for other chlorinated organics.

The high resolution gas chromatography/electron impact mass spectrometry (HRGC/MS) analysis of these effluent extracts was performed using selected ion monitoring. The analytical conditions used were:

Column: 30 m x 0.25 mm fused silica column, wall-coated with DB-5
Column Temperature: 100°C (1 min hold) to 325°C at 10°C/min
Injector: Grob-type, 45 s splitless, 280°C
Electron Energy: 70 eV

C. Selection of Compounds for Evaluation

1. PCBs

Five repeat experiments were performed in which the feed oil was PCB-spiked mineral oil. In three of these experiments (runs 90-92), the mineral oil (Exxon HPLX 355077) was spiked with 50 µg/g each of 2,3,5,6-tetra-, 3,3',4,4',5,5'-hexa-, and 2,2',4,4',6,6'-hexachlorobiphenyl. These compounds were purchased from Ultra Scientific. Runs 90-92 were performed under the same conditions as run 26 reported from the previous work. In two experiments (runs 97 and 98), the mineral oil (Exxon HPLX 355077) was spiked with 50 µg/g of Aroclor 1254 (Monsanto). These two runs are duplicates of runs 45 and 46 from the previous work.

2. Chlorobenzene

A chlorobenzene dielectric fluid was fed during two runs (runs 106 and 107). This chlorobenzene fluid (Electro-Chem FR-15, Standard Chlorine Chemical Company in Kearny, NJ) was determined to contain mostly trichlorobenzene isomers with some tetrachlorobenzene. This is the same chlorobenzene fluid which was previously tested as runs 57 and 58.

Table 1. Operating Conditions for Phase IV Tests

Feed material	Run no.	Combustion temperature (°C)	Run time (min)	Excess oxygen (%)	Residence time (s)	CO_2 (%)	CO (%)	Combustion efficiency (%)	Pyrolysis temperature (°C)
PCB congeners	11-14-90-M+M+M	678	58	7.9	0.80	0.22	0.37	37	397
PCB congeners	11-14-91-M+M+M	678	60	7.9	0.81	0.21	0.40	34	397
PCB congeners	11-16-92-M+M+M	678	61	7.9	0.79	0.27	0.29	48	397
None	11-16-93-MO(B)[a]	677	55	7.9	0.79	0.07	0.0005	99	397
Tetrachloroethylene	11-19-94-WEC	676	60	7.8	0.80	0.08	0.03	70	397
Tetrachloroethylene	11-20-95-WEC	676	57	8.0	0.79	0.07	0.01	85	397
None	11-20-96-WEC(B)[a]	676	56	8.0	0.80	0.06	0.0005	99	397
Aroclor 1254	11-28-97-M50	677	61	7.9	0.82	0.12	0.32	27	397
Aroclor 1254	11-28-98-M50	677	57	8.0	0.81	0.12	0.33	26	397
Mineral oil	11-29-99-MO[b]	678	61	7.9	0.79	0.13	0.52	19	397
OCDF	11-30-100-OCDF	678	37	7.9	0.81	0.14	0.33	29	397
OCDF	11-30-101-OCDF	679	35	7.9	0.78	0.15	0.33	30	398
OCDF	11-30-102-OCDF(B)	677	55	7.9	0.77	0.06	0.0003	99	398
HTH (para)	12-3-103-HTH(P)	676	44	7.9	0.79	0.09	0.09	47	444
HTH (ester)	12-4-104-HTH(E)	677	45	8.0	0.81	0.12	0.21	35	444
None	12-4-105-HTH(B)	676	45	8.0	0.81	0.07	0.0002	99	445
Trichlorobenzene	12-5-106-CLBZ	677	16	7.8	0.79	0.08	0.16	32	397
Trichlorobenzene	12-5-107-CLBZ	677	16	8.1	0.78	0.07	0.16	29	397
None	12-5-108-CLBZ(B)	677	61	7.9	0.78	0.07	0.0009	98	397

[a]Runs with "(B)" suffixes are blank runs with no feed.
[b]Mineral oil with no PCBs added.

3. Wecosol®

This dielectric fluid, containing tetrachloroethylene (> 99%), was also tested on runs 94 and 95. It was obtained from Westinghouse Corporation, Pittsburgh, PA.

4. HTH

Two high temperature hydrocarbon dielectric fluids were tested on runs 103 and 104. The first type of fluid is a paraffinic hydrocarbon [designated HTH(P) in run 103] labeled "RTEmp®." It was obtained from RTE Corporation, Waukesha, WI. The other fluid is an esterified hydrocarbon [designated HTH(E) in run 104]. It was labeled "Dielectric fluid HT-310-S" and was obtained from Standard Chlorine Chemical Company, Kearny, NJ.

5. Octachlorodibenzofuran

Two runs were completed (runs 100 and 101) using a feed which consisted of 500 µg/g of octachlorodibenzofuran (OCDF) from Ultra Scientific in mineral oil (Exxon HPLX 355077). It was apparent from the previous work that a variety of PCDF congeners are formed from many precursors in the thermal combustion system. It was not apparent from this work, the available literature, or communication with other researchers, whether these PCDFs were formed directly from precursors or whether a highly chlorinated dibenzofuran (e.g., heptaCDF or octaCDF) was first formed and then dechlorinated. It was decided that using a feed oil spiked with OCDF could provide insight about the chemistry of PCDF formation.

IV. RESULTS AND DISCUSSION

A. Continuous Monitoring Results

Table 1 lists the thermal combustion system operating conditions for the tests completed during this phase of the program. This table shows the combustion temperatures, the percent excess oxygen measured in the combustion effluent, the calculated residence time, the percent CO_2 and percent CO measured in the combustion effluent, the calculated combustion efficiency, and the pyrolysis temperature.

B. PCB-Containing Matrices

1. PCB Isomers

In three runs (Nos. 94, 95, 96), the feed oil consisted of mineral oil spiked with 500 µg/g each of the three PCB isomers 2,3,5,6-tetra-, 3,3'4,4',5,5'-hexa-, and 2,2',4,4',6,6'-hexachlorobiphenyl (replicates of run 26 in the previous work). The results of analysis of PCDFs in these runs are listed in Table 2. Table 3 lists the conversions of PCBs to PCDFs. The literature (Buser et al. 1978; Buser and Rappe 1979) suggests that each of the three PCB isomers produces specific PCDF isomers as shown below:

Table 2. PCDF Formation from PCB-Spiked Mineral Oil

Run no.	MonoCDF (ng)	DiCDF (ng)	TriCDF (ng)	TetraCDF (ng)	PentaCDF (ng)	HexaCDF (ng)	HeptaCDF (ng)	OctaCDF (ng)	PCDFs[a] (ng)
11-14-90-M+M+M	770	550	2,100	1,400	240	73	< 20[b]	< 10	5,100
11-14-91-M+M+M	810	520	4,500	2,600	320	< 30	< 20	< 10	8,800
11-16-92-M+M+M	810	< 5	3,200	2,000	830	280	< 20	< 10	7,100
11-16-93-MO(B)[c]	< 5	< 5	< 5	82	73	85	110	12	360
11-28-97-M5O	-[d]	-	-	250	30	< 30	< 20	< 10	280
11-28-98-M5O	-	-	-	190	20	31	16	< 10	240
11-29-99-MO	-	-	-	< 10	< 10	< 30	< 20	< 10	0

[a] The not detected values (< X) were considered to be zero for calculating total PCDF concentration.
[b] Not detected; estimated method quantitation limit is given.
[c] Runs with "(B)" suffixes are blank runs with no feed.
[d] - = Not analyzed.

Table 3. Percent Conversion PCB to PCDF

Run no.	MonoCDF Conversion efficiency (%)	DiCDF Conversion efficiency (%)	TriCDF Conversion efficiency (%)	TetraCDF Conversion efficiency (%)	PentaCDF Conversion efficiency (%)	HexaCDF Conversion efficiency (%)	HeptaCDF Conversion efficiency (%)	OctaCDF Conversion efficiency (%)	Total PCDF (%)
11-14-90-M+M+M	NC[a]	NC	0.61	0.20	0.035	0[b]021	NC	NC	0.37
11-14-91-M+M+M	NC	NC	1.14	0.37	0.046	0[b]	NC	NC	0.85
11-16-92-M+M+M	NC	NC	0.88	0.29	0.12	0.077	NC	NC	0.39
11-28-97-M50	-[c]	-	-	0.69	0.082	0	0	0	0.77
11-28-98-M50	-	-	-	0.55	0.058	0.091	0.047	0	0.70

[a]NC = Not calculated; conversion efficiencies only calculated for proposed reaction mechanisms.
[b]0 = not detected.
[c]- = not analyzed

2,3,5,6-Tetrachlorobiphenyl $\xrightarrow[O_2]{\Delta}$ 1,2,4-Trichlorodibenzofuran

3,3',4,4',5,5'-Hexachlorobiphenyl $\xrightarrow[O_2]{\Delta}$ 2,3,4,6,7,8-Hexachlorodibenzofuran

2,2',4,4',6,6'-Hexachlorobiphenyl $\xrightarrow[O_2]{\Delta}$ 1,3,7,9-Tetrachlordibenzofuran + 1,3,4,7,9-Pentachlorodibenzofuran

The conversion efficiencies listed in Table 3 assume the above reactions apply. As noted in the previous report, only one isomer each of triCDF and tetraCDF was present in the samples. However, several pentaCDF and hexaCDF isomers were identified, indicating that either the chemistry of the PCB-to-PCDF conversion is more complex than originally thought or the PCDFs are degrading and rearranging after the initial formation. A total PCB to total PCDF conversion is also listed for each run in Table 3. No PCDDs were detected in these samples.

The PCDF formations in the three M+M+M runs (90, 91, and 92) were similar. The results are also in agreement with those previously obtained under these experimental conditions (Table 14 in Erickson et al. 1984). Although the current results are not as high as those in the previous report, they are higher than the amounts observed under any other experimental conditions. Thus, the current results corroborate the conclusion reached in the previous report that combustion at 675°C for 0.8 s with 8% excess oxygen is optimum for formation of PCDFs from PCBs.

The combustion effluents from these PCB-spiked mineral oil runs (Nos. 90, 91, and 92) were also analyzed for PCBs. From these results, the PCB destruction efficiencies were calculated for each run using the formula presented in the previous report. The destruction efficiencies are shown in Table 4. These results (91, 93, and 85%) compare well with the previously reported destruction efficiencies (Table 30 in Erickson et al. 1984).

2. Aroclor 1254

In two runs (97 and 98) the feed oil consisted of mineral oil spiked with 50 µg/g of Aroclor 1254 (Monsanto Corporation). These runs duplicate runs 45 and 46 from the previous work. The results of the analysis of PCDFs in these runs are also shown in Table 2. These results are generally comparable to those previously reported. The calculated conversion efficiencies for PCB to PCDF are shown in Table 3. No PCDDs were found in the samples. A conversion efficiency is given for each PCDF homolog. Unlike the conversion efficiencies calculated in individual PCB isomers, these conversion efficiencies were calculated using the total concentration of Aroclor 1254 feed. Figure 2 shows a plot of the nanograms of each PCDF homolog detected in these runs per milliliter of spiked mineral oil feed versus homolog. This figure combines the data from this phase of work with a similar graph from the previous report (Figure 22 in Erickson et al. 1984). The overall formation efficiency is similar to that previously reported. However, the PCDF distribution in the current work tends toward higher chlorination.

Table 4. PCB Destruction Efficiencies for PCB-Spiked Mineral Oil

Run no.	Destruction efficiency (%)
11-14-90 M+M+M	81
11-14-91 M+M+M	93
11-16-92 M+M+M	85
11-28-97 M50	73
11-28-98 M50	72

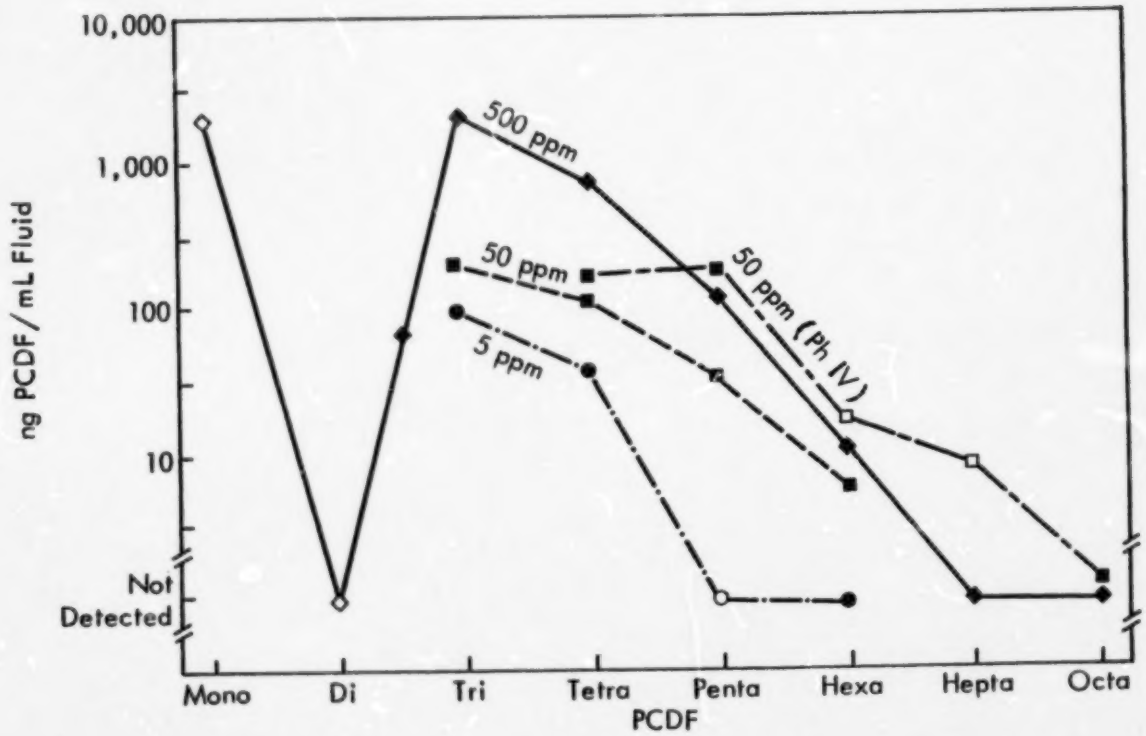

Figure 2. PCDF formation in PCB-spiked mineral oil by homolog (Phase III and Phase IV results). Closed symbols are averages of two values; open symbols are single determinations; missing points are no data. Phase IV data are superimposed on Phase III data, previously published as Figure 22 in Erickson et al. (1984).

The combustion effluent from the Aroclor 1254-spiked feed runs (Nos. 97 and 98) was also analyzed for PCBs. The PCB destruction efficiency was calculated as described in the previous report. These results are shown in Table 4. These two calculated destruction efficiencies (73 and 72%) compare well with the calculated destruction efficiencies reported previously (Table 30 in Erickson et al. 1984).

C. Non-PCB Dielectric Fluids

1. Chlorobenzene Fluid

In runs 106 and 107 the feed was a non-PCB containing chlorobenzene dielectric fluid (RF-15 from Standard Chlorine Chemical Company). These runs duplicate runs 57 and 58 from the previous work. The major compounds identified in the analysis of the combustion effluents include dichloro-, trichloro-, tetrachloro-, pentachloro-, and hexachlorobenzene. No PCBs were detected in chlorobenzene combustion effluents.

The results of the analysis of PCDFs in these runs are shown in Table 5. The PCDF levels detected for runs 106 and 107 are higher than previously reported (runs 57 and 58 in Erickson et al. 1984). However, several concentrations in the previous report are "greater than" values; hence, comparison is difficult.

Table 6 lists the amounts of PCDDs formed from these chlorobenzene dielectric fluid runs. The total amount and overall distribution of PCDDs detected are comparable to the levels previously reported (runs 57 and 58 in Erickson et al. 1984). Figure 3 shows a plot of the nanograms of each PCDF and PCDD homolog detected in these runs per milliliter of chlorobenzene fluid fed versus homolog. Figure 4 combines these data with a similar plot from the previous report (Figure 25 in Erickson et al. 1984). The isomeric distributions of the PCDFs and PCDDs in these runs were similar to those from the previous runs (see Figure 20 in Erickson et al. 1984).

2. Wecosol®

As shown in Table 5 and Figure 5, fairly consistent amounts of tetraCDF through octaCDF were formed from thermal reaction of Wecosol®. While the conversion efficiency (Figure 1) is low relative to pure PCBs, it does correspond roughly to the PCDF formation from 500 ppm Aroclor 1254 (Erickson et al. 1984). Low amounts of hexa- through octaCDD were observed (Table 6) in the Wecosol® runs. However, only slightly lower amounts of the PCDDs were found in the run immediately following the two Wecosol® runs. Therefore, the significance of the PCDD values cannot be determined from these data.

Figures 6 and 7 present extracted ion current profiles of the PCDFs. The isomeric distribution from the tetrachloroethylene precursor is slightly different from those previously observed from reaction of PCBs or trichlorobenzene (Figures 10-20 in Erickson et al. 1984).

Table 5. PCDF Formation from Non-PCB Dielectric Fluids and OCDF

Run no.	MonoCDF (ng)	DiCDF (ng)	TriCDF (ng)	TetraCDF (ng)	PentaCDF (ng)	HexaCDF (ng)	HeptaCDF (ng)	OctaCDF (ng)	PCDFs (ng)
11-19-94-WEC	-[a]	-	-	630	600	920	1,100	270	3,500
11-20-95-WEC	-	-	-	2,400	2,400	1,800	1,500	320	8,400
11-20-96-WEC(B)[b]	-	-	-	< 10	91	140	150	42	420
11-30-100-OCDF	-	-	-	3,600	6,200	29,000	41,000	14,000	94,000
11-30-101-OCDF	-	-	-	3,700	4,300	42,000	50,000	20,000	120,000
11-30-102-OCDF(B)	-	-	-	170	120	190	260	150	890
12-3-103-HTH(P)	-	-	-	33	< 10	25	35	62	160
12-4-104-HTH(E)	-	-	-	< 10	< 10	< 30	40	< 10	40
12-4-105-HTH(B)[c]	-	-	-	1,100	1,500	1,000	340	80	4,020
12-5-106-CLBZ	1,100	5,900	32,000	79,000	93,000	9,800	19	< 10	220,000
12-5-107-CLBZ	570	1,700	3,700	32,000	48,000	22,000	690	70	109,000
12-5-108-CLBZ(B)[c]	84	140	240	610	960	1,300	1,300	750	5,400

[a] - = Not analyzed.
[b] Runs with suffixes "(B)" are blank runs with no feed.
[c] Extracted after the OCDF and CLBZ samples (Run Nos. 11-30-100-OCDF, 11-30-101-OCDF, 12-5-106-CLBZ, and 12-5-101-CLBZ). Observed PCDFs may be carryover in glassware or carryover in thermal combustion system.

Table 6. PCDD Formation from Non-PCB Dielectric Fluids and OCDF

Run no.	MonoCDD (ng)	DiCDD (ng)	TriCDD (ng)	TetraCDD (ng)	PentaCDD (ng)	HexaCDD (ng)	HeptaCDD (ng)	OctaCDD (ng)	PCDDs (ng)
11-19-94-WEC	-[a]	-	-	< 10	< 10	57	130	120	310
11-20-95-WEC	-	-	-	< 10	< 10	51	72	49	170
11-20-96-WEC(B)[b]	-	-	-	< 10	< 10	< 30	72	46	120
11-30-100-OCDF	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
11-30-101-OCDF	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
11-30-102-OCDF(B)	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
12-3-103-HTH(P)	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
12-4-104-HTH(E)	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
12-4-105-HTH(B)	-	-	-	< 10	< 10	< 30	< 20	< 10	< 80
12-5-106-CLBZ	24	40	1,100	600	< 10	< 30	< 20	< 10	1,800
12-5-107-CLBZ	81	150	350	680	63	94	< 20	< 10	1,400
12-5-108-CLBZ(B)	< 5	< 5	< 5	< 10	< 10	< 30	< 20	< 10	< 100

[a] - = Not analyzed.
[b] Runs with suffixes "(B)" are blank runs with no feed.

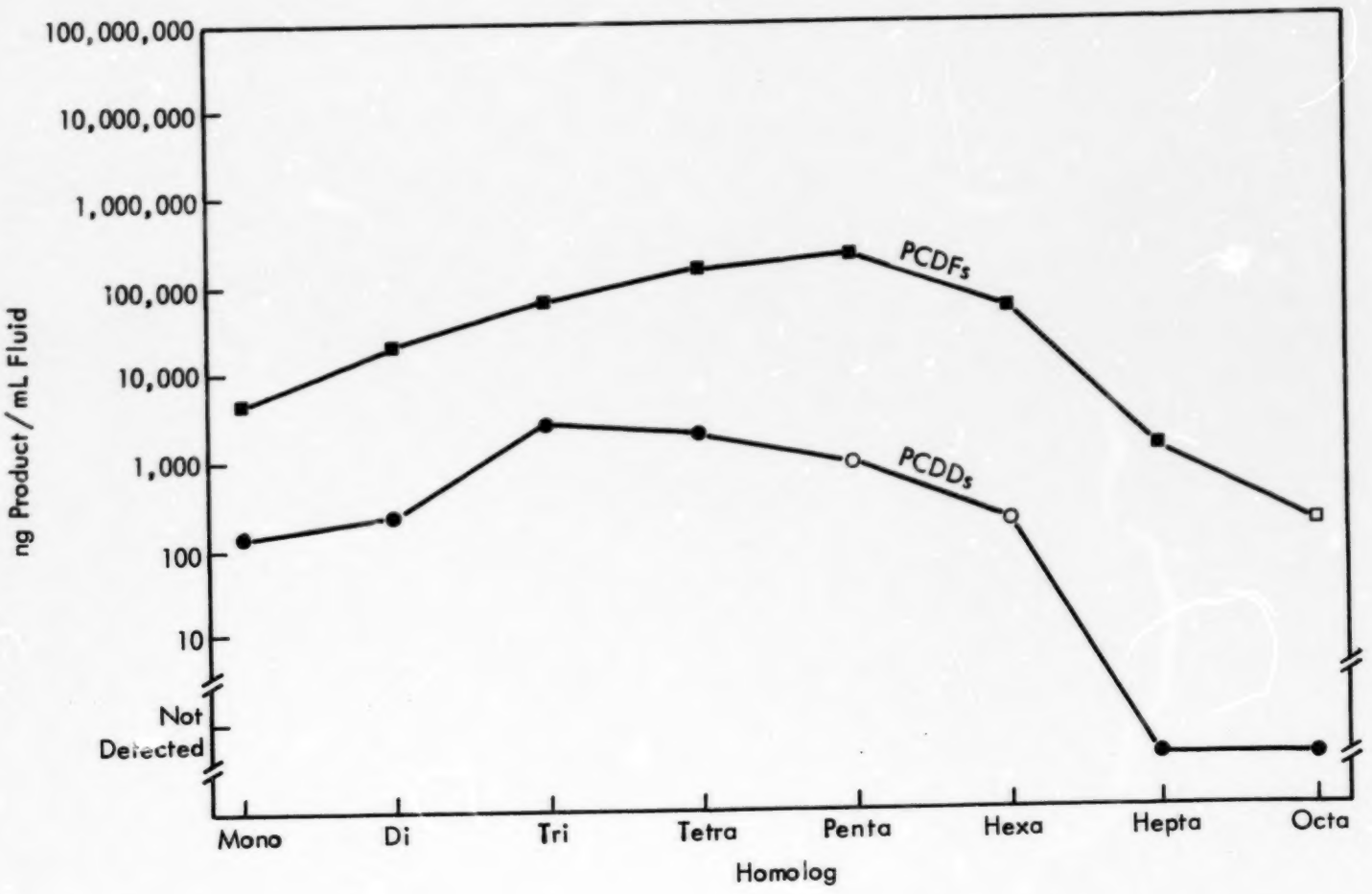

Figure 3. PCDF and PCDD formation from trichlorobenzene transformer fluid (Phase IV results). Closed symbols are averages of two values; open symbols are single determinations.

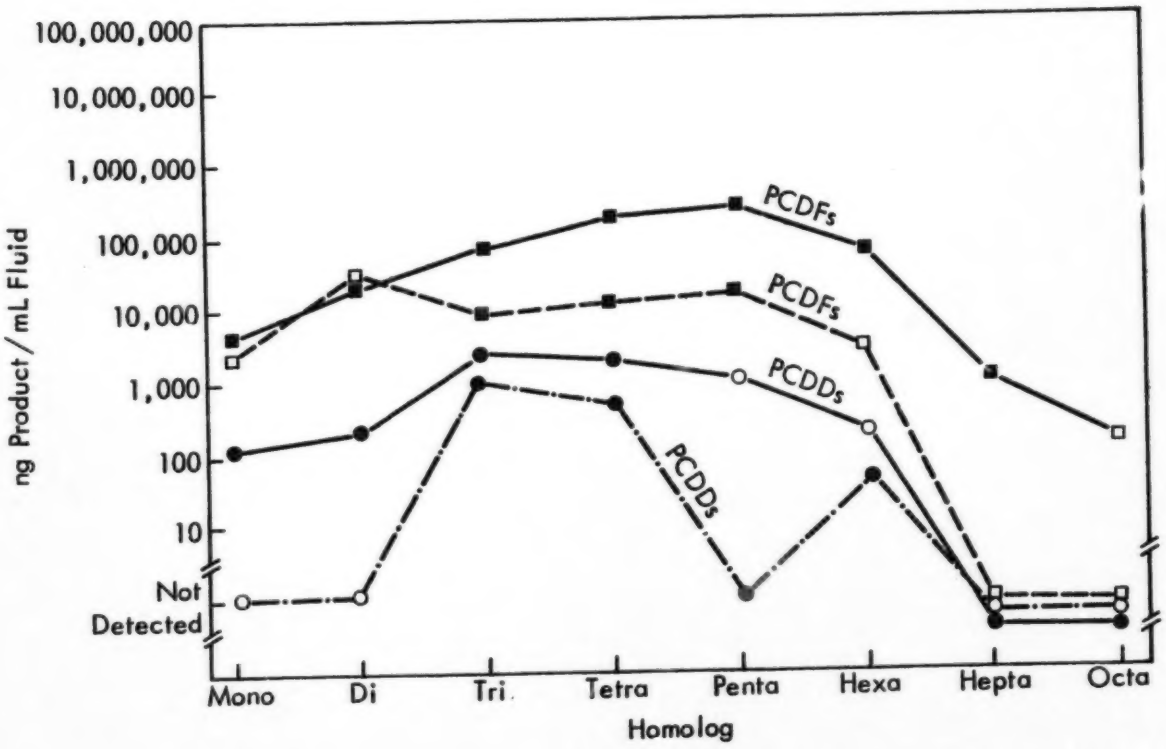

Figure 4. PCDF and PCDD formation from trichlorobenzene transformer fluid (Phase III and Phase IV results). Solid lines are Phase IV results; broken lines are Phase III results, originally published as Figure 25 in Erickson et al. (1984). Closed symbols are averages of two values; open symbols are single determinations.

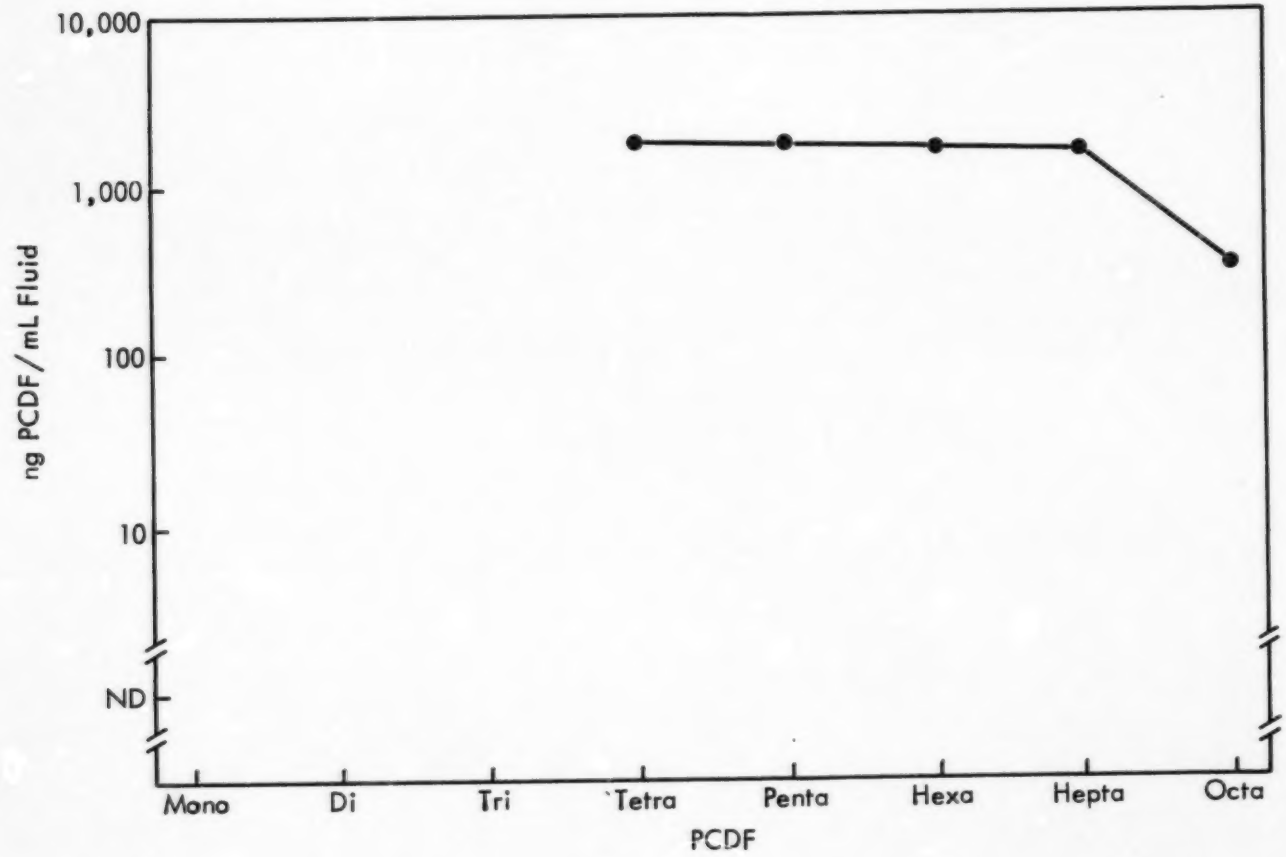

Figure 5. PCDF formation from Wecosol®. Closed symbols are averages of two values; missing points are no data.

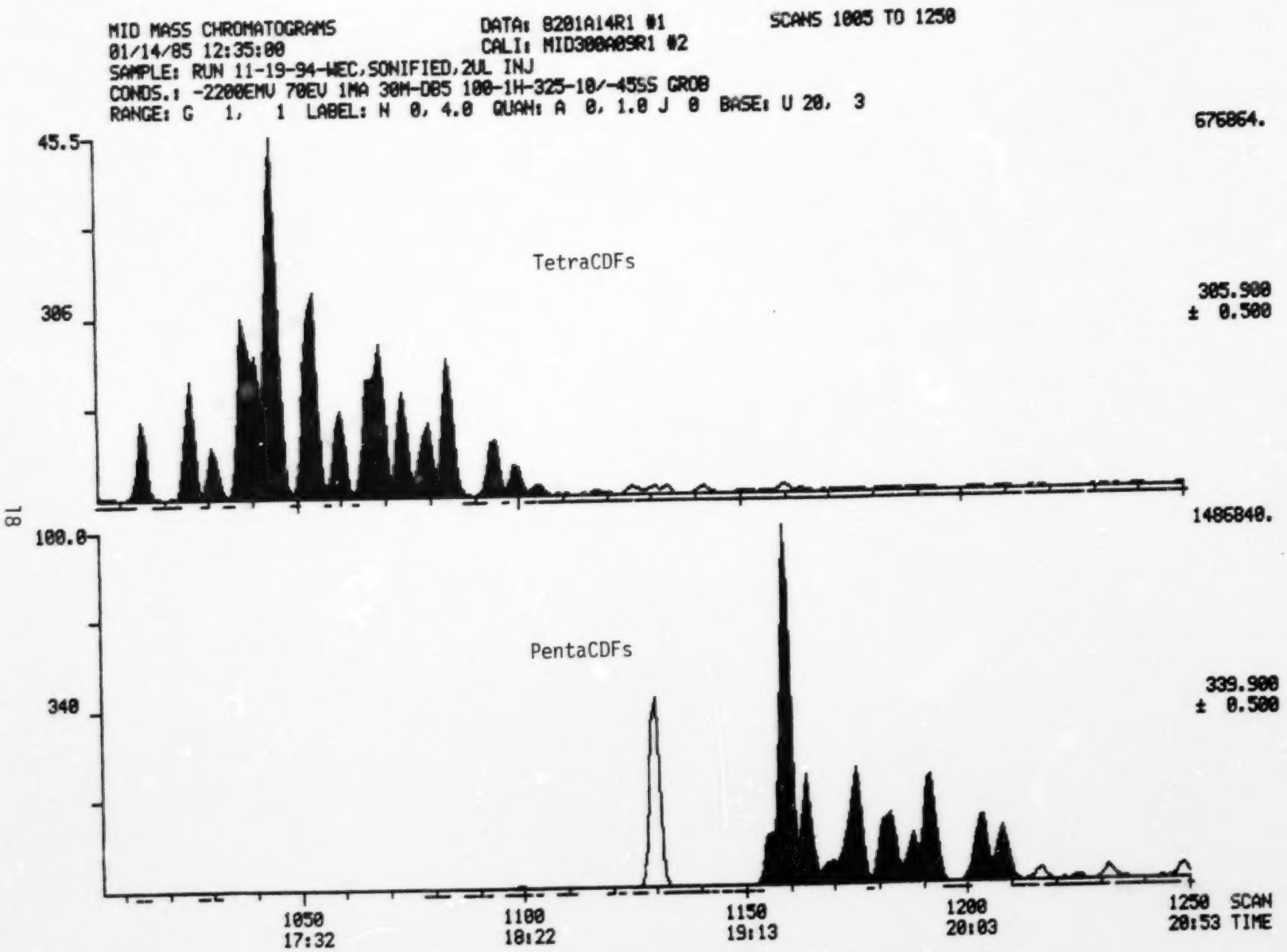

Figure 6. Tetra- and PentaCDFs in sample 11-19-94-WEC.

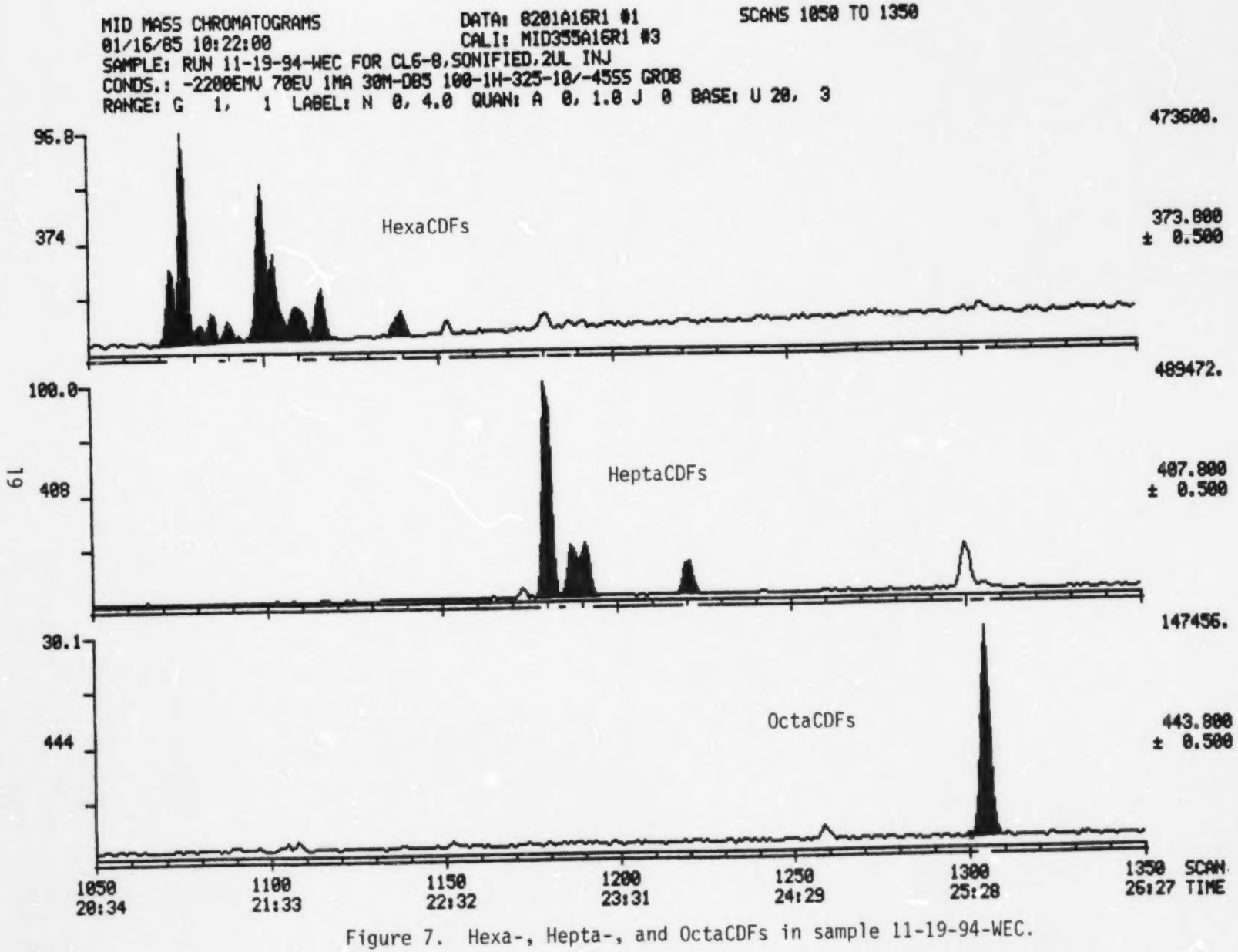

Figure 7. Hexa-, Hepta-, and OctaCDFs in sample 11-19-94-WEC.

These samples were also analyzed by full scan HRGC/MS. A large amount of tetrachloroethylene was observed. Chlorinated benzenes were also observed. A variety of nonchlorinated compounds were also identified, including smaller polynuclear aromatics, hydrocarbons, phthalate esters, and aldehydes. A more detailed identification of these products will be reported at a later date.

3. HTH

No appreciable amounts of PCDFs or PCDDs were found in the reaction products of HTH (ester) or HTH (para) runs, listed in Tables 5 and 6. The small amounts of PCDFs found in run 103 were apparently carryover from the previous OCDF runs. This conclusion is supported by the fact that the isomer patterns in the HTH and OCDF runs were similar.

These samples were also analyzed by full scan HRGC/MS. A variety of C_8-C_{20} hydrocarbons, smaller polynuclear aromatics and their alkyl adducts, aliphatic alcohols, aldehydes and ketones were observed. A more detailed identification of these products will be reported at a later date.

4. Octachlorodibenzofuran

Two runs, followed by a blank run, were conducted with OCDF in mineral oil at 500 µg/mL. As discussed in Section III.C.5, the objective of these experiments was to assess the potential for formation of lower chlorinated homologs from OCDF. As noted in Table 5 and Figure 8, substantial amounts of the lower PCDF homologs were formed. Only about 8% of the OCDF feed passed through the reaction system unchanged. No PCDDs were detected (Table 6). Preliminary, nonquantitative analyses indicated that small amounts of mono- through triCDFs were also formed.

Figures 9 and 10 present extracted ion current profiles of the PCDFs formed from the OCDF feed. The isomeric distribution of the PCDFs has some similarities to those observed from combustion of tetrachloroethylene (Figures 6 and 7), PCBs, or trichlorobenzene (Figures 10-20 in Erickson et al. 1984). Further work is needed to identify specific similarities and differences.

D. Quality Assurance and Quality Control

A variety of QA and QC activities were conducted throughout the course of this work to assure that the results were acceptable. The project records were inspected by MRI's Quality Assurance Unit and any deficiencies were corrected. The data were spot-checked by the work assignment leader and reviewed by the Quality Assurance Unit.

Various routine QC activities were conducted to provide data on the data quality. All thermal combustion runs were conducted in duplicate (see Tables 2, 5, and 6) to provide a measure of precision. Isotopically labeled compounds were added to assess the overall accuracy. The recovery of ^{13}C-TCDD averaged 66 ± 23% for 16 samples, based on external standards. Similarly, recoveries for ^{13}C-TCDF averaged 69 ± 17% and ^{13}C-OCDD averaged 45 ± 15% (14 samples). The differences in number of samples arose from interferences in certain samples which prevented quantitation of one or more of the surrogates.

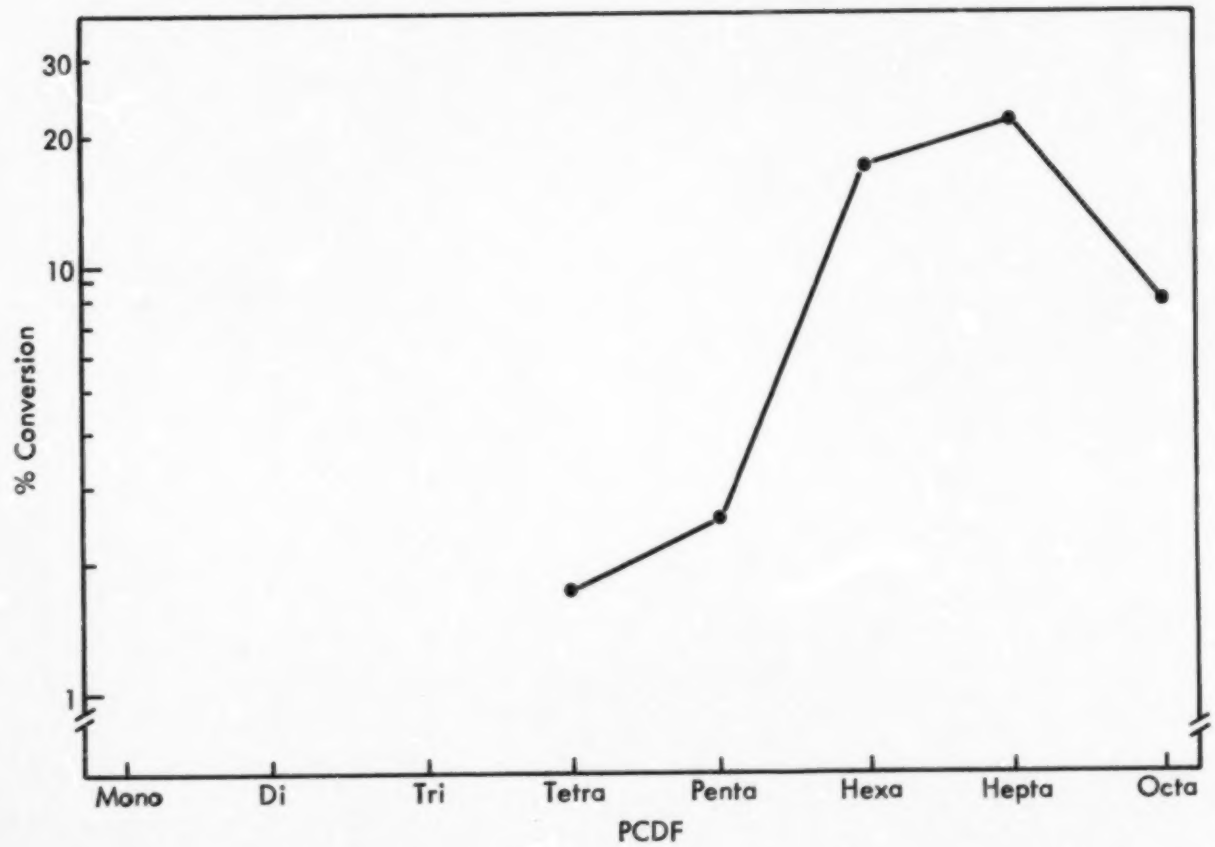

Figure 8. PCDF formation from OCDF-spiked feed, expressed as percent of OCDF fed into system. Closed symbols are averages of two values; missing points are no data.

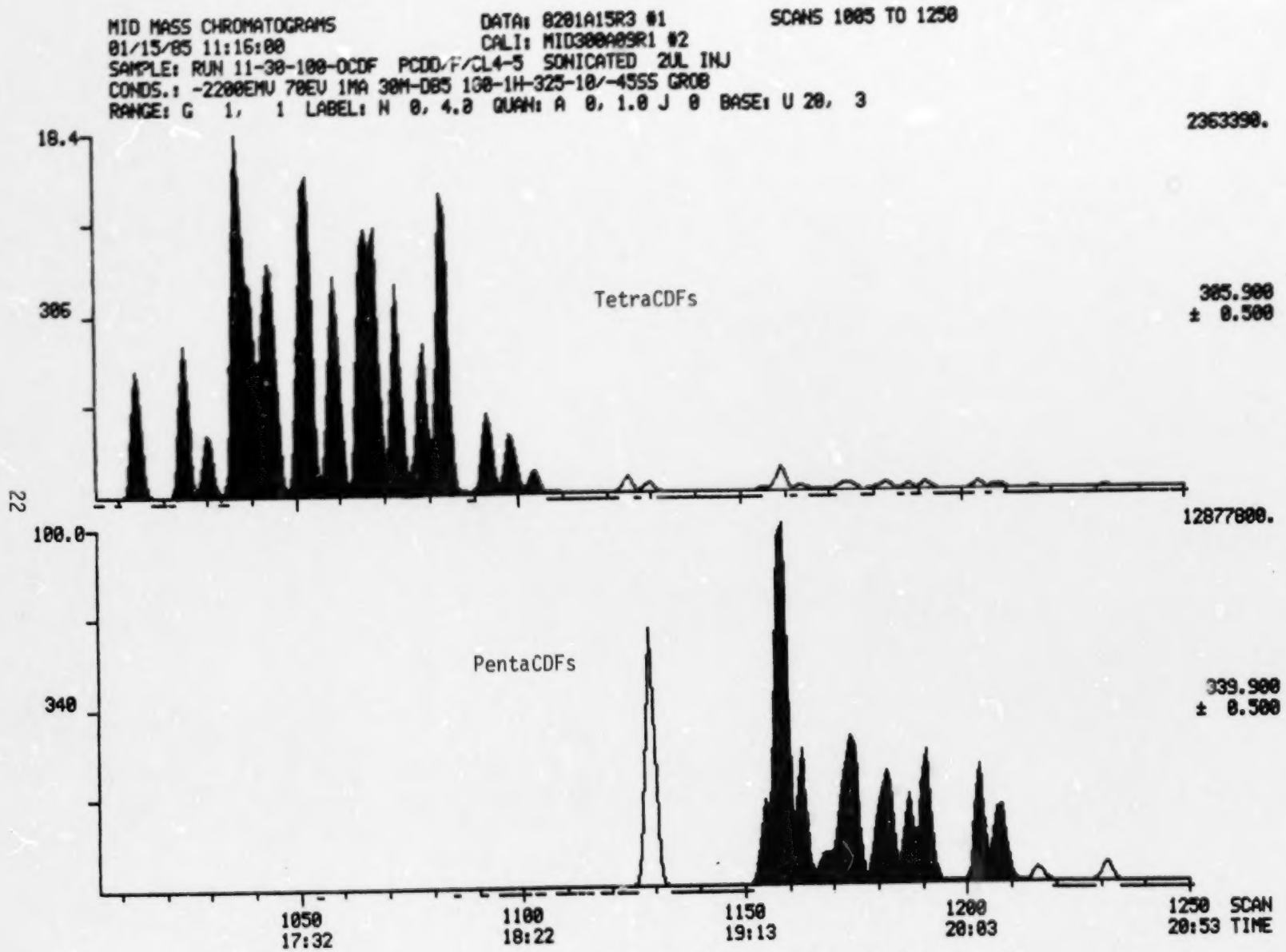

Figure 9. Tetra- and PentaCDFs in sample 11-30-100-OCDF.

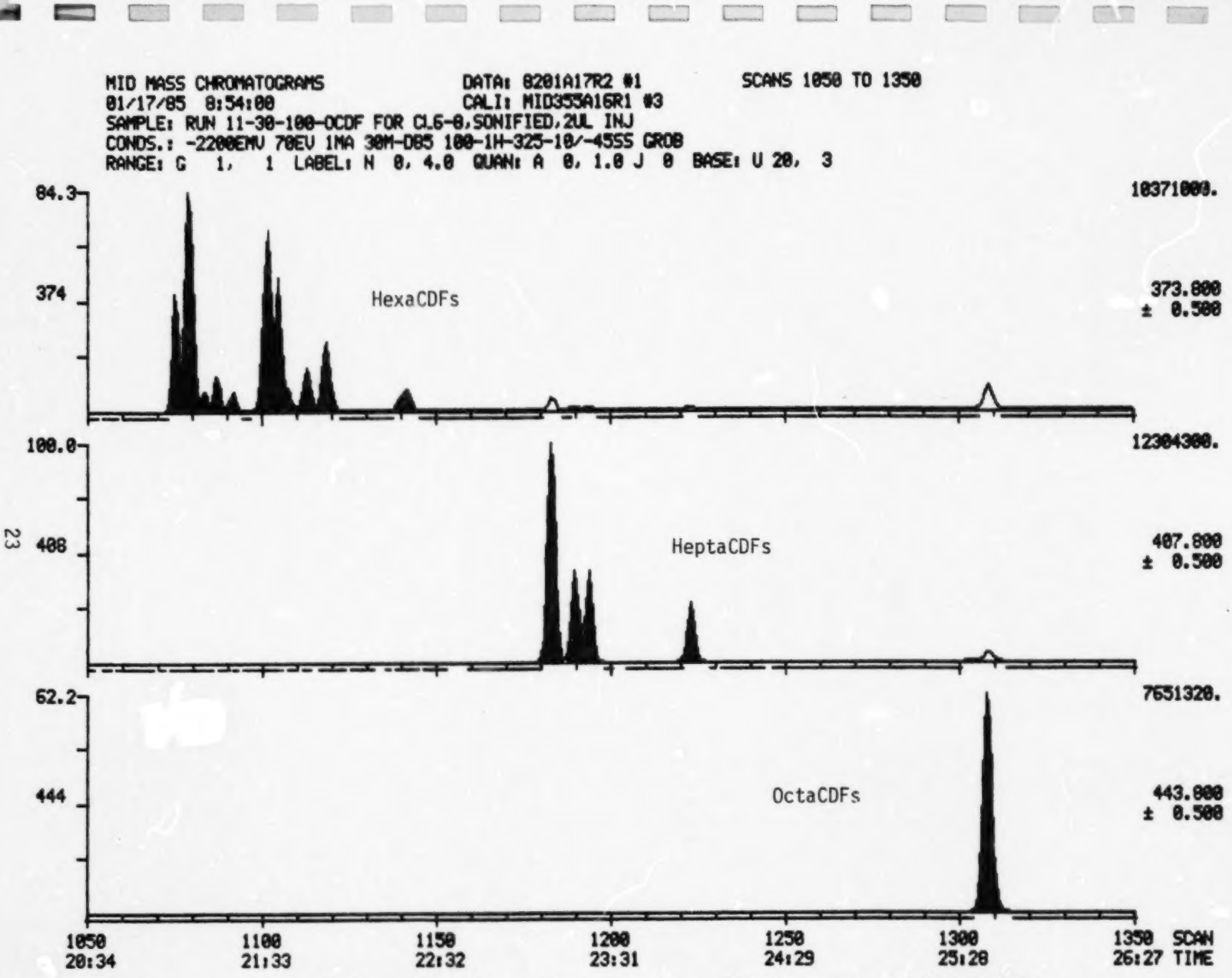

Figure 10. Hexa-, Hepta-, and OctaCDFs in sample 11-39-100-OCDF.

The values for the native PCDFs and PCDDs presented in this report have been corrected for the surrogate recovery, as described in the Chemical Analysis Section in the previous report (Erickson et al. 1984).

V. REFERENCES

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